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(54) Title: MULTIFUNCTIONAL CYANATE ESTER AND EPOXY BLENDS (57) Abstract A curable resin blend including a multifunctional phenolic cyanate/phenolic triazine copolymer, and an epoxy resin, and articles manufactured therefrom is disclosed. The cured resin blend possesses a high glass transition temperature, excellent mechanical properties such as flexural strength, elongation, flexural modulus, compressive strength and compressive modulus, as well as a low moisture absorption. The cured blend is suitable for making laminates, coatings, composites, and molds such as via resin transfer molding, compression molding, and the like.		

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MULTIFUNCTIONAL CYANATE ESTER AND EPOXY BLENDS

Background Of The Invention1. Field of the Invention

The invention relates to certain novel blends of phenolic cyanate-phenolic triazine copolymers and epoxy resins, as well as to articles prepared from said blends. More particularly, the invention relates to such blends which have improved properties.

2. Prior Art

Phenolic resins are a class of synthetic materials which greatly vary in molecular structure. Therefore, a multitude of applications for these products exists as a result of the array of physical properties that arise from the synthetic options. However, phenolics disadvantageously exhibit less than desirable thermal oxidative stability and produce an extensive, uncontrollable amount of volatile by-products during cross-linking.

In order to obviate certain of the disadvantages attendant to phenolics, U.S. Patent No. 4,970,276 proposed a modified multifunctional phenolic cyanate/phenolic triazine copolymer ("PT resin") which had greater oxidative, mechanical, and thermal stability as compared to conventional phenolic resins, and did not produce volatile by-products during crosslinking. Further, these PT resins possessed better elongation properties and higher glass transition temperatures than the conventional phenolic resins. Additional examples of such PT resins are described in U.S. Patent Nos. 4,970,276, 4,978,727, and 5,126,412.

Another approach for producing thermosettable blends having improved mechanical properties is by blending dicyanate esters with epoxy resins as

disclosed in U.S. Patent Nos. 4,612,359, 4,506,603, 4,477,629, 4,546,131, 4,487,915, and 3,562,214, and in Shimp, et al., "Co-Reaction of Epoxide and Cyanate Resins," 33rd Int'l SAMPE Symposium and Exhibition 1 - 13 (Calif. March 7 - 10, 1988) and Shimp, AroCy® Cyanate Ester Resins Chemistry, Properties & Applications, (3rd Ed. May, 1991). These blends have been useful in the production of base materials for printed circuits as disclosed in Patent Nos. DE 4,022,255, DD 290,844, DE 4,125,420, and DE 4,224,835.

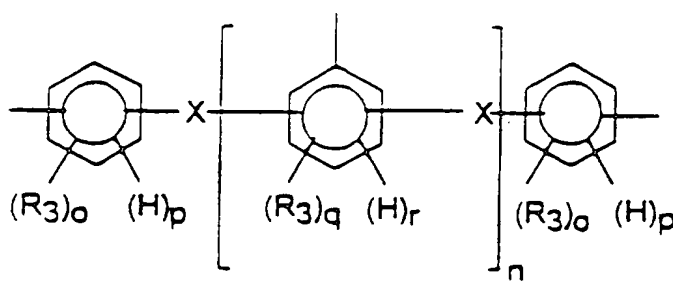
Although the above inventions provide thermosettable resin blends which, when cured, possess excellent thermal stability and mechanical properties, there is room for additional improvement in the overall mechanical properties, especially in glass transition temperature, as well as in water absorption.

It would be desirable to provide a thermosettable resin blend which, when cured, is superior to prior art phenolic resins and dicyanate blends in one or more of the properties selected from glass transition temperature, flexural strength, flexural modulus, elongation, and water absorption.

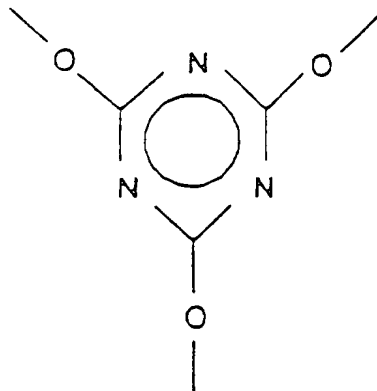
Summary Of The Invention

In accordance with this invention, there is provided a blend comprising:

- a) a multifunctional phenolic cyanate/phenolic triazine copolymer comprising three or more phenolic moieties of formula I:



linked by way of at least one of the open valences to one or more triazine moieties of the formula II:



II

and wherein the remainder of the open valences of said phenolic moieties are substituted with -OH, -OCN, or other triazine moieties, provided that at least one of said remaining open valences is substituted with a -OCN moiety; wherein:

n is a positive whole number equal to or greater than 1;

q and r are the same or different at each occurrence and are whole numbers from 0 to 3 with the proviso that the sum of q and r at each occurrence is equal to 3;

o and p are the same or different at each occurrence and are whole numbers from 0 to 4, with the proviso that the sum of o and p is equal to 4;

-X- is a divalent organic radical; and

R_3 is the same or different at each occurrence and is a substituent other than hydrogen which is unreactive under conditions necessary to completely cure the copolymer; and

b) an epoxy resin.

Another aspect of the invention pertains to the article resulting from curing

the aforementioned blend with a curing quantity of a curing agent, catalyst or mixture of curing agent and catalyst therefor.

The blend of the invention and the products resulting therefrom exhibit one or more beneficial properties, such as, improved glass transition temperature and water absorption.

Description Of The Preferred Embodiments

Component a of the present invention includes multifunctional phenolic cyanate/phenolic triazine copolymer resins or "PT resins" having at least three phenolic moieties of the formula I linked by at least one of said open valences to one or more triazine moieties of the formula II. The remainder of said open valences being substituted with -OCN, -OH or other triazine moieties, provided that at least one of said remaining open valences is substituted with a -OCN group, wherein R_3 , n, q, r, o, p, and X are as described above.

In the structure of formula I, R_3 is an inert substituent. Illustrative of suitable R_3 groups are such inert substituents as halo, trihalomethyl, alkyl, alkoxy, phenyl, and the like.

In the structure of formula I, -X- is a divalent organic radical. Illustrative of suitable -X- groups are alkylene such as methylene, ethylmethylene, 2-ethylpentylmethylene, methylmethylene, isopropylmethylene, isobutylmethylene, pentylmethylene, furylmethylene, and the like; arylenes such as 1,3-benzenedimethylene, phenylmethylene, 1,4-benzenedimethylene, 2,2-bis-(4-phenylene)propane, 4,4-diphenylene dimethylenethane and the like; and cycloalkylenes such as cyclohexylene, cyclooctylene, 1,3-cyclohexanedimethylene,

and the like.

In the preferred embodiments of the invention:

-X- is a substituted or unsubstituted methylene or 1,4-benzenedimethylene wherein permissible substituents are alkyl or furyl;

5 q and r are the same or different at each occurrence and are positive whole numbers from 0 to 3, with the proviso that the sum of q and r is 3;

R₃ is alkyl;

n is from 1 to about 20; and

10 o and p are the same or different at each occurrence and are positive whole numbers from 0 to 4, with the proviso that the sum of o and p is 4;

 wherein up to about 30 mol percent of the phenyl moieties of said copolymer are substituted with said triazine moieties, up to about 90 mol percent of said phenyl moieties are substituted with -OH groups and up to about 90 mol percent of said phenyl moieties are substituted with -OCN groups, said mol
15 percent being based on the total mols of phenyl groups in said copolymer. Unless indicated otherwise, all references herein are in terms of weight percent.

 Among the preferred embodiments of the invention, particularly preferred are those embodiments of the invention in which:

20 from about 2 to about 25 mol percent of said phenyl groups of the PT resin are substituted with triazine moieties, from about 40 to about 90 mol percent of said phenyl groups are substituted with -OCN groups and from about 2 to about 50 mol percent of said phenyl groups are substituted with -OH groups, said mol percent based on the total mols of phenyl group in said copolymer;

-X- is methylene, methylene substituted with alkyl having from about 1 to about 10 carbon atoms, halo or furfuryl, or xylene;

R_3 is methyl or ethyl;

o is 0 or 1;

5 n is from about 1 to about 10;

q is 0 or 1;

r is 2 or 3;

p is 3 or 4.

10 Among these particularly preferred embodiments, most preferred are those embodiments wherein:

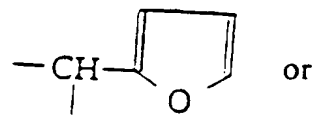
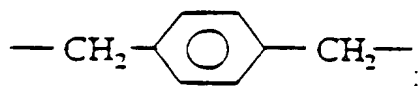
n is 3 to about 10;

from about 5 to about 20 mol percent of the phenyl groups of the phenyl triazine/phenyl cyanate copolymer are substituted with -OCN groups and from about 5 to about 20 mol percent of said phenyl groups are substituted with -OH groups, said mol percent being based on the total mols of phenyl groups in said copolymer;

q is 0;

o is 0;

X is a moiety of the formula: $-\text{CH}_2-$, $-\text{CF}_2-$,

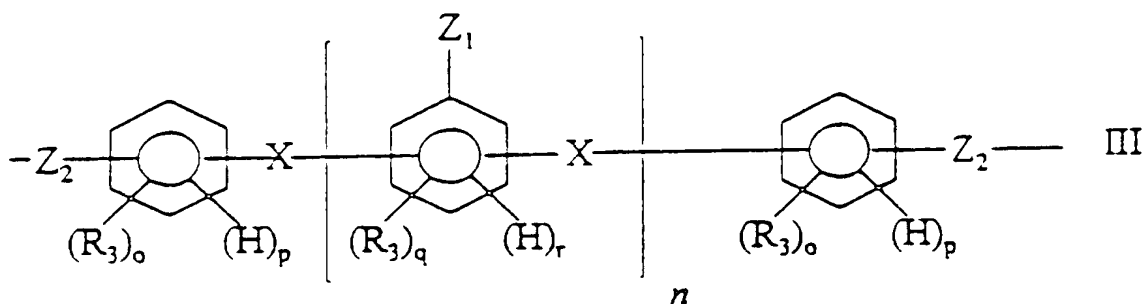


20 r is 3; and p is 4.

Especially good results are obtained in the practice of the invention where

from about 10 to about 20 mol percent of the phenyl groups in the PT resin are substituted with triazine moieties, from about 10 to about 20 mol percent of said phenyl groups are substituted with -OH groups and from about 60 to about 80 mol percent of said phenyl groups are substituted with -OCN groups, said mol percent
 5 being based on the total mols of phenyl groups in said copolymer.

These especially preferred copolymers are preferably linear copolymers having recurring units of the formula III:



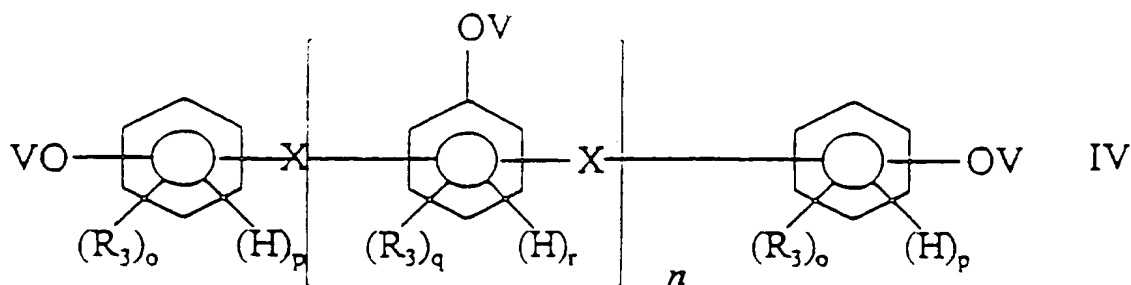
wherein R_3 , o , p , q , r , $-X-$, and n are as described above and wherein:

Z_1 is -OH or -OCN at each occurrence;

10 Z_2 is a trivalent triazine moiety;

with the proviso that from about 10 to about 20 mol percent of the phenyl groups of the copolymer are substituted with trivalent triazine moieties, from about 70 to about 75 mol percent of phenyl groups are substituted with -OCN groups, and from about 10 to about 20 mol percent of the phenyl groups are
 15 substituted with -OH groups, said mol percent based on the total mols of phenyl groups in the copolymer.

Suitable materials which can be employed in the preparation of the phenolic cyanate resin precursor to the PT resin of component a include phenolic salts of formula IV:

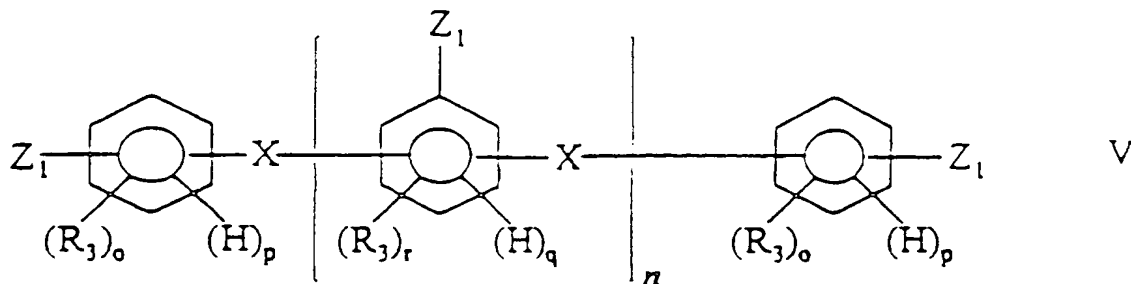


wherein R_3 , q , r , o , p , n , and X are as described above, and V is hydrogen or a cation of an organic or inorganic base which is formed by reaction between said base and the protons of a phenol to form the corresponding basic salt, wherein the mol ratio of cations to hydrogen are sufficient to form the desired mol percent of -

5 OCN groups in the desired phenolic cyanate.

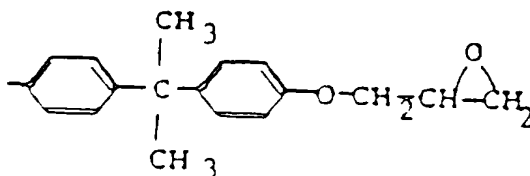
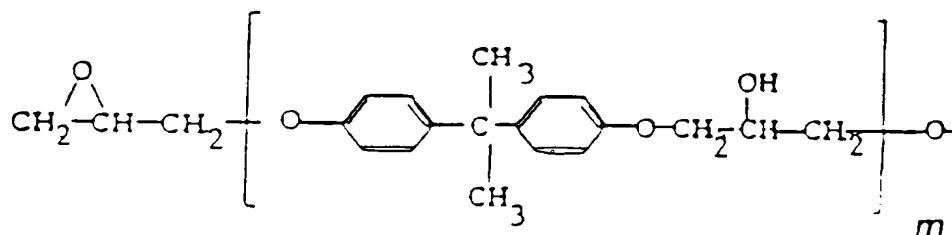
These phenolic salts react with cyanogen halides via a nucleophilic displacement reaction in order to produce the phenolic cyanate resin precursor used in the preparation of the PT resins of component a, details of which are disclosed in U.S. Patent No. 4,970,276, which is incorporated by reference herein.

10 PT resins suitable for use in component a of the blend of the present invention may be prepared by the known method of controlled "polycyclotrimerization" of the phenolic cyanate precursor having formula V:



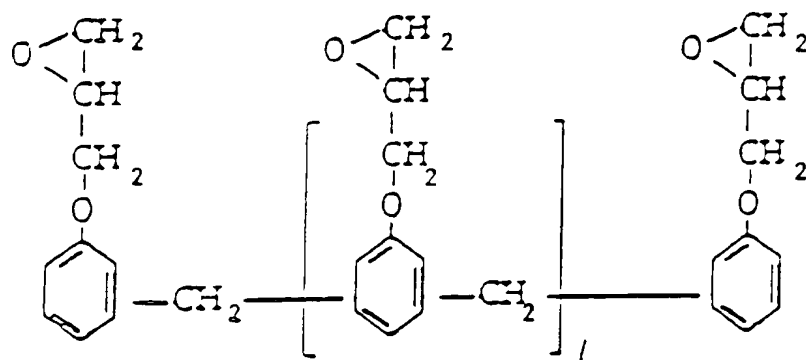
to the extent necessary to form the desired mol percent of trivalent triazine moieties, wherein R_3 , n , q , r , o , p , Z_1 , and X are as described above, provided that the amount of Z_1 group which are $-OCN$ is sufficient to provide the desired mol percent of triazine moieties and $-OCN$ moieties in the desired copolymer. Details of the method for PT resin production are also described in U.S. Patent No. 4,970,276.

Suitable epoxy resins for blending with the PT resin include bisphenol A based epoxy resins, halogenated epoxy resins, epoxy novolac resins, polyglycol epoxy resins, and mixtures and copolymers thereof. Illustrative of suitable bisphenol A based epoxy resins include compounds of the following formula:



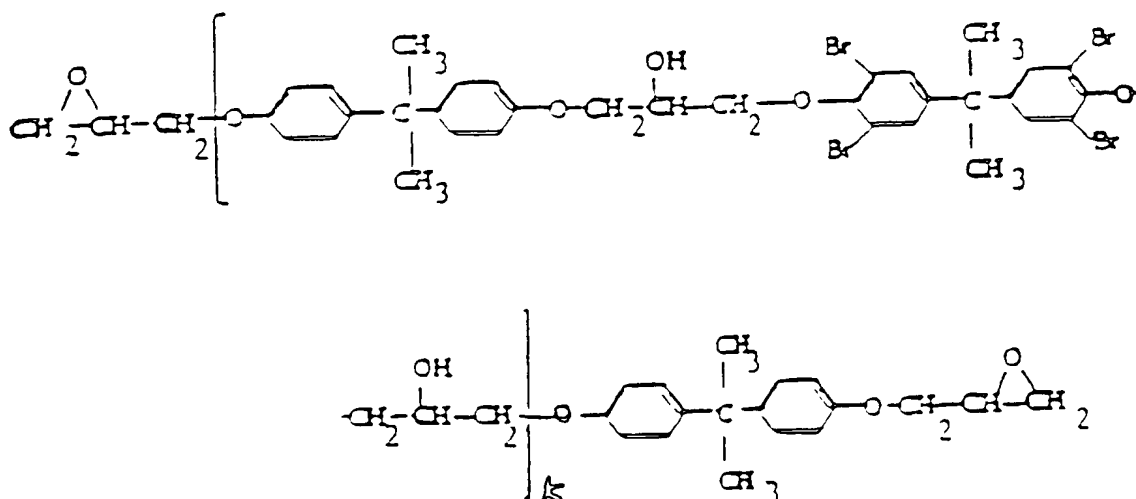
wherein the average value of m is from about 0.1 to about 1, preferably about 0.1 to about 0.2.

Illustrative of suitable epoxy novolac resins include compounds of the following formula:

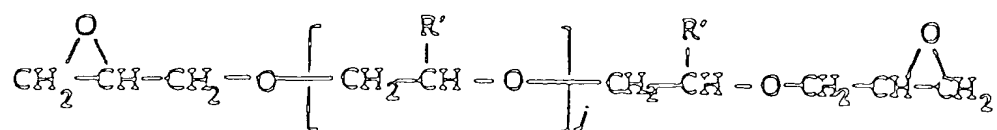


wherein the average value of l is from about 0.1 to about 2, preferably about 0.1 to about 0.3.

Suitable halogenated epoxy resins include those epoxies substituted with chlorine, bromine, fluorine, and mixtures thereof. Illustrations of suitable brominated epoxy resins include compounds of the following formula:



wherein the average value of k is from about 2 to about 3, preferably about 2 to about 2.5. Illustrations of suitable polyglycol epoxy resins include compounds of the following formula:

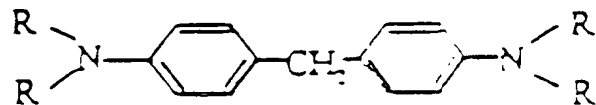


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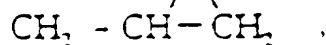
wherein the average value of j is from about 1 to about 2, preferably about 1.9 to about 2.0, and R' is a hydrogen or an organic group, such as an alkyl group having from about 1 to about 5 carbons. These epoxy resins can be obtained from commercial sources, e.g., from The Dow Chemical Company.

Other suitable epoxy resins include multifunctional epoxy resins, such as tetra- and tri-functional epoxy resins, which may be used alone, or mixed or copolymerized with the above-described epoxy resins. As used herein, "multifunctional epoxy resin" means a resin which may contain greater than about 1 to about 4, preferably 3 to about 4 epoxy groups, more preferably 4 epoxy groups. Illustrations of such tetra-functional and tri-functional multifunctional

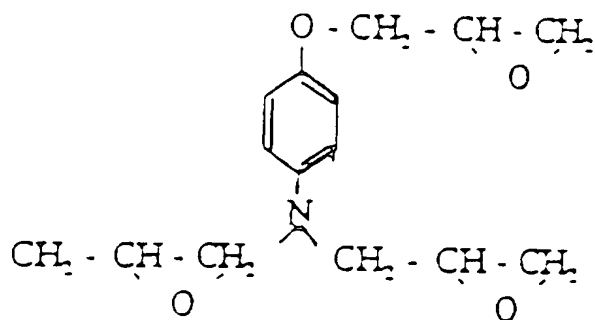
epoxy resins are



, wherein R is



and



respectively, which can be obtained from commercial sources, e.g., from Ciba-Geigy Corporation under the tradename "Araldite".

In a preferred embodiment, an epoxy having, based upon the total weight of the epoxy resin, from about 15 percent to about 45 percent, preferably about 8 percent to about 12 percent, bromination is employed. Unless indicated otherwise, all references herein are with respect to weight percent. As the amount of brominated epoxy resin in the blend of the present invention is increased, various properties, such as adhesion and glass transition temperature ("T_g") also increase.

In an alternative embodiment wherein a blend having a low viscosity is desired, the incorporation of a polyglycol epoxy resin is preferred.

The blend of the present invention includes a mixture of, based upon the total weight of the blend, from about 5 to about 95 percent, preferably from about 15 to about 50 percent, and more preferably about 25 to about 30 percent PT resin with from about 5 to about 95 percent, preferably about 25 to about 70 percent, epoxy resin.

The blend of the present invention may optionally contain, based upon the total weight of the blend, from about 0 to about 20, preferably about 3 to about 10 percent, of a multifunctional epoxy resin in addition to the amount of epoxy resin or resins employed in component b. Examples of suitable multifunctional epoxy resins include those described above. When a blend having high T_g and adhesion properties is desired, it is preferred that such multifunctional epoxy resins are used as a third component in the blend of the present invention.

The blend of the present invention may also optionally contain a catalyst for the purpose of increasing the cure rate of the blend. The amount of the

catalyst employed depends largely on the type of the catalyst, the curing conditions, and/or the use of the final cured product. Usually, the blend of the present invention contains, based upon the total weight of the blend, from about 0.01 percent to about 0.2 percent, preferably 0.08 percent to about 0.11 percent of a catalyst.

Suitable catalysts employed herein are the primary catalysts and/or the organic catalysts or "curing agents". Illustrations of the primary catalysts include, for example, transition metal salts of aliphatic and aromatic carboxylic acids, nitrogen and phosphorus compounds. Particularly suitable catalysts include, for example, lead naphthenate, manganese naphthenate, manganese octoate, manganic acetylacetonate, cobalt octoate, cobalt naphthenate, cobalt acetylacetonate, zinc octoate, zinc naphthenate, zinc acetylacetonate, copper acetylacetonate, cupric naphthenate, nickel acetylacetonate, titanyl acetylacetonate, ferric octoate, tin octoate, diazabicyclo[2.2.2]octane, catechol, 1,1-dimethyl-3-phenylurea, mixtures thereof and the like. Manganese octoate is most preferred. These catalysts are obtainable from commercial sources, e.g., from Aldrich Chemical Company, Inc., and Pfaltz & Bauer, Inc.

Other suitable catalysts include organic catalysts or curing agents, such as alkyl phenols, imidazoles and mixtures thereof. These organic catalysts or curing agents are employed for the purpose of further accelerating the cure, and may be used alone or in combination with the above-mentioned metal catalysts.

Preferable organic catalysts may be selected from the group consisting of nonylphenol, 1-methyl-imidazole, 2-ethyl-4-methylimidazole, 2-phenylimidazole,

and 2-methylimidazole ("2-MI"), with 2-MI being most preferred. These organic catalysts are also obtainable from commercial sources, e.g., from Aldrich Chemical Company, Inc.

5 In a preferred embodiment, based upon the total weight of the blend, from about 0.025% to about 0.06% of manganese octoate with about 0.06% to about 0.07% 2-MI may be employed.

If desired, the blend, i.e., the PT resin and/or epoxy resin component, can be blended with other compounds, such as solvents, fillers, mold release agents, pigments, dyes, flow modifiers, combinations thereof and the like. Examples of
10 such compounds are described in U.S. Patent No. 4,496,695, which is incorporated herein by reference.

Suitable such solvents include, for example, aromatic hydrocarbons, ketones, halogenated hydrocarbons, combinations thereof and the like. Particularly suitable solvents include, for example, dimethylformamide,
15 tetrahydrofuran, acetone, 1-methyl-2-pyrrolidinone, methylethylketone, methylene chloride, combinations thereof and the like.

The PT resin and/or epoxy resin may contain fillers for use in where the structural strength and integrity of a structure has to be maintained, and for other purposes known to those of skill in the art. Any suitable filler known to those of
20 skill in the art may be used. Such fillers may be selected from a wide variety of organic and inorganic materials such as polymers, minerals, metals, metal oxides, siliceous materials, and metal salts. Illustrative of useful fillers are kevlar fibers, rock-wool, slag wool, fiberglass, phenolic fibers, aramide, boron, and carbon fibers,

as well as plate-like, fibrous and particulate forms of alumina, brass powder, aluminum hydrates, iron oxide, feldspar, lead oxides, asbestos, talc, barytes, calcium carbonates, clay, carbon black, quartz, novaculite and other forms of silica, kaolinite, aluminum silicate, bentonite, garnet, mica, saponite, baddeleyite, calcium
5 oxide, fused silica, calcium hydroxide, synthetic fibers such as paper, pulp, wood flour, cotton, linter and polyimide fibers, and the like. Other useful fillers include thermoplastic polymers, as for example, polyesters, polyimides, polyamides, polysulfones, polyaramids, polyester carbonates, polyphenylene ether, polyethersulfones, polyethylene, polypropylene, polycarbonates, polyetherimides,
10 polysulfides, polyacrylates, polyvinyls and the like. Methods for producing reinforced and/or filled blends include melt blending, extrusion and molding processes, simple mixing and dispersion of both materials in suitable medium by methods known in the art.

For coloring purposes, a curable resin blend of this invention may include
15 white pigments such as titanium dioxide, and coloring pigments or various organic dyes and pigments, such as lead yellow, carbon black, iron black, molybdenum red, prussian blue, navy blue, cadmium yellow, and cadmium red.

The curable resin blends of the present invention may be prepared by either a wet process or a dry process, both of which are conventionally known in
20 the art. Choice of the process is determined by the proportion of components and final use of the blend.

In the wet process, each component is individually dissolved in a solvent, then all of the components are blended so as to obtain a curable resin blend

having the desired proportion. Alternatively, at least one of the components is dissolved in a solvent, and the other components are added thereto. In view of the high viscosity of both the PT resin and epoxy, it is preferred that, when selecting the latter embodiment, at least these two components are initially
5 dissolved in a solvent before other components are added thereto. Otherwise, it may be necessary to heat the PT resin-epoxy mixture to temperatures ranging from about 65°C to about 75°C in order to lower the viscosity and improve the mixing thereof, and thus reduce the likelihood of non-uniformities in the end product.

The blends prepared according to the wet process contain a solvent or
10 solvents. The solvent may be removed by heating the blend or by keeping the blend under a reduced pressure.

Solvents suitable for dissolving the components employed in the wet process include, for example, ketones, such as acetone, methyl ethyl ketone, and the like, as well as tetrahydrofuran, methylene chloride, dimethylformamide, 1-methyl-2-
15 pyrrolidinone, and the like.

According to the dry process, the PT resin and epoxy resin components are continuously mixed via conventional means at temperatures of about 65°C to about 75°C until homogeneous. An effective amount of a solution comprised of from about 15 to about 25 percent, based upon the total weight of the solution, of
20 catalyst predissolved in an alkyl phenol solvent, such as nonylphenol, dodecylphenol, o-cresol, 2-sec-butylphenol and 2,6-dinonylphenol, most preferably nonylphenol, may optionally be added thereto such that the amount of catalyst in the homogeneously blended blend is from about 0.06 to about 0.07 percent, based

upon the total weight of the blend. The resulting blend is continuously stirred for about 20 minutes to about 1 hour until homogeneous.

Further details regarding both the wet process and the dry process are described in "Formulating with Dow Epoxy resins Electrical Laminates" by The Dow Chemical Company (Feb. 1990).

The method of curing the resin blend of this invention is not restricted in particular. Usually it is performed by heating. Generally a temperature of about 18°C to about 400°C, preferably a temperature of about 100°C to about 300°C, is selected. The time required for curing differs depending upon the form in which the resin blend of this invention is used, i.e., depending on whether it is a thin film, or a relatively thick molded article or laminate. Usually, a period sufficient for curing the resin may be selected from the range of from about 1 hour to about 2 hours. When the resin blend of this invention is to be used in molded articles, such as those produced via resin transfer molding, compression molding, injection molding, and the like, laminates or bonded structures, it is desirable to apply pressure during the heat curing mentioned above.

Other curing methods involve use of microwave, radio frequency, ionizing radiation, electron beams from various types of accelerators, gamma-rays from isotopes such as cobalt 60, sunlight, and active energy, for example, light radiated from a light source such as a tungsten lamp, or a low-pressure or high-pressure mercury lamp. In the case of photocuring, the resin blend of this invention may contain up to 5 percent, based upon the total weight of the blend, of a known photosensitizer, for example, an organic carbonyl compound such as benzoin,

benzoin methyl ether, benzanthrone, anthraquinone and benzophenone, or a combination of a sensitizing dye such as eosine, erythrosine or acridine with an amine. Such a photocurable resin blend containing a photosensitizer is effective in coating applications.

5 The blends of the present invention are preferably employed to prepare articles including, but not limited to, composites and laminates, i.e., electrical laminates such as printed circuit boards or rigid substances suitable for the production of printed circuit boards. In preparing the boards, one or more plies, preferably about 4 to about 8 plies, of a fibrous substrate are coated and/or
10 impregnated with the blend of the present invention and laminated. Conventional coating equipment can be employed. Subsequent to coating and/or impregnating and laminating, the substrate is cured at a temperature of about 100°C to about 300°C for about 1 hour to about 2 hours to form a rigid substrate. The blends can be used to coat and/or impregnate fibrous substrates such as fiberglass, nylon,
15 paper such as that obtainable from DuPont under the tradename "Thermount", polyimides, graphite, and the like. The substrate can be in the form of woven fabric, mat, monofilament, multifilament rovings, and the like.

 The ratio of the blend of the present invention to the substrate in a prepreg may vary from, based upon the total weight of the preimpregnated substrate or
20 "prepreg", about 20:80 to about 50:50, and preferably from about 35:65 to about 40:60. As used herein, "prepreg" shall refer to the substrate coated with the uncured resin blend of the present invention.

 After the rigid substrate is formed, at least one ply, preferably 1 to about 2

plies, of a sheet of copper or other electrically conductive material, e.g., gold, silver, aluminum and the like, can then be laminated to the rigid substrate using laminating conditions such as pressure of about 0.34 MPa to about 2.76 MPa and temperatures of about 50°C to about 300°C applied for about 30 to about 300 minutes. Then a circuit can be etched into the conductive layer using techniques well-known to form circuit boards.

The following non-limiting examples are presented to further illustrate the present invention.

The following properties of the blends produced in the Examples were determined as follows:

a) The glass transition temperatures were determined by using differential scanning calorimetry ("DSC") via the method described in Interconnecting Packaging Circuitry 2.4.25 (1986)("IPC"), as well as by using thermal mechanical analysis ("TMA") via the method described in IPC 2.4.24.

b) The flammability was determined via the method described in the Underwriters Laboratory UL94 Flame Test.

c) The dielectric constant and dissipation factor was determined via the methods described in ASTM D-5109, respectively, using 5.1 cm by 5.1 cm by 0.07 cm specimens at 1 MHz.

d) The percent water absorption was determined via the dip in method described in IPC 2.6.2.1 at temperatures of 23°C and 100°C, respectively, using specimens having a thickness of 0.07 cm for Examples 1 to 3 and Comparative Examples 1 to 3, and via the method described in ASTM-D570, at a temperature

of 23°C using specimens having a thickness of 0.32 cm for Examples A - C.

e) The flexural modulus was determined via the method described in ASTM-D790, using 1.3 cm x 7.6 cm x 0.32 cm specimens.

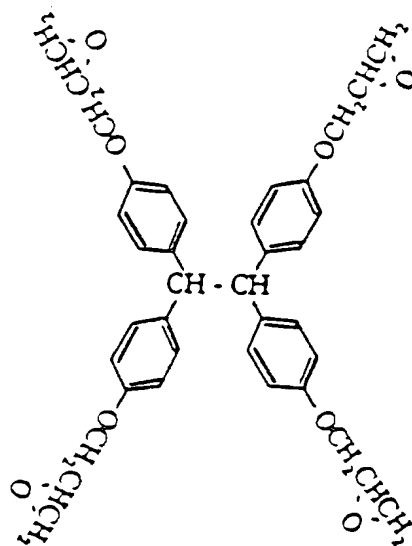
f) The compressive strength was determined via the method described in ASTM-D695, using 0.635 cm x 0.635 cm x 1.905 cm specimens.

The following components are employed in the Examples:

Component A is a cyanate ester resin available from AlliedSignal Inc., Morristown, New Jersey under the tradename "Primaset", having a molecular weight of about 480, a viscosity at 80°C of about 0.3 Pa·S to about 0.35 Pa·S and a gel time of 15 to 20 minutes at 200°C.

Component B is a brominated epoxy resin available from The Dow Chemical Company having an epoxide equivalent weight ("EEW") of about 425 to about 440, a bromine content of about 20 percent by weight, and a viscosity at 25°C of about 1.5 Pa·S to about 2.5 Pa·S.

Component C is a tetrafunctional epoxy resin available from Shell Chemical Company under the tradename "Epon 1031" having the following formula:



and an EEW of about 200 to about 240.

Component D is a brominated epoxy resin available from The Dow Chemical Company under the tradename "DER 592" having an EEW of about 345 to about 375, a bromine content of about 17 percent by weight, and a viscosity at
5 171°C of about 0.8 Pa·S.

Component E is a tetrafunctional epoxy resin available from Ciba-Geigy Corporation under the tradename "MY-720", having an EEW of about 117 to about 134 and a viscosity at 50°C of about 8 to 18 Pa·S.

Component F is an epoxy novolac resin available from The Dow Chemical
10 Company under the tradename "DEN 431", having an EEW of about 172 to about 179, and a viscosity at 52°C of about 1.1 to about 1.7 Pa·S.

Component G is a liquid Bisphenol-A type epoxy resin available from The

Dow Chemical Company under the tradename "DER 331", having an EEW of about 182 to about 192, an average molecular weight of about 378, and a viscosity at 25°C of about 11 to about 14 Pa·S.

Component H is a catalytic solution of manganese octoate (6 percent active manganese) in mineral spirits available from Pfaltz & Bauer, Inc.

The relative amounts of Components A, B, C, and D, as used in Examples 1 to 3 and Comparative Examples 1 to 3 are illustrated in Table I. The relative amounts of Components A, E, F, G, and H as used in Examples A, B, and C and Comparative Examples A and C are illustrated in Table II.

Table I

	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3
Component % by weight						
A	20.5	24.19	26.0			
B	59.81	45.44		59.80	45.44	
C		7.63	8.03		7.62	8.03
D			48.9			48.84
BADCY				20.49	24.20	25.96
% Br by weight in blend	12.0	9.1	8.3	12.0	9.1	8.3

Table II

	Example A	Comp. Example A	Example B	Example C	Comp. Example C
Component % by weight					
A	49.98		49.97	49.97	
E	49.98	53			
F			49.97		
G				49.97	43
BADCY		47			57
H	0.049		0.054	0.058	

Example 1: Substrate Coated With Blend**of PT Resin and Brominated Epoxy Resin**

About 328 parts of PT30 resin (Component A) is dissolved in about 313 parts of acetone in a 3.79 liters tin container. To this mixture is added about 957 parts of brominated epoxy resin (Component B), followed by, based upon the total weight of the mixture, about 0.03 percent of a catalytic solution of manganese octoate (6% active manganese) in mineral spirits and about 0.07% of 2-MI under room temperature conditions, and then the resulting mixture is stirred for about 2 hours until homogeneous.

A glass fabric is then impregnated with the resulting mixture and cured at 177°C with 1.03-1.38 MPa pressure for 15 minutes, and then for about 1 hour at 220°C under the same pressure conditions.

Example 2: Substrate Coated With Blend of PT
Resin, Epoxy Resin With 20% Bromination, and
Tetrafunctional Epoxy Resin

About 395 parts by weight of PT30 resin (Component A) is dissolved in
5 about 239 parts of acetone. To this mixture are added about 741 parts by weight
of brominated epoxy resin (Component B) and about 125 parts by weight of
tetrafunctional epoxy resin (Component C), followed by, based upon the total
weight of the mixture, about 0.024 percent of a solution of manganese octoate
(6% active manganese) in mineral spirits and 0.064% of 2-MI under room
10 temperature conditions, and then the resulting mixture is stirred for about 2 hours
until homogeneous.

A glass fabric substrate is then impregnated with the resulting blend and
cured in the same manner and under the same pressure conditions as described in
Example 1.

15 Example 3: Substrate Coated With Blend of PT Resin, Epoxy
Resin With 17% Bromination, and Tetrafunctional Epoxy Resin

About 390 parts by weight of a PT30 resin (Component A) is dissolved in
about 255 parts of acetone. To this mixture are added about 735 parts of a
brominated epoxy resin (Component D) and about 121 parts by weight of a
20 tetrafunctional epoxy (Component C), followed by, based upon the total weight of
the mixture, about 0.04% of the catalytic solution of Example 1 under room
temperature conditions, and then the resulting mixture is stirred for about 2 hours
until homogeneous.

A glass fabric substrate is then impregnated with the resulting blend and cured in the same manner and under the same conditions described in Example 1.

Comparative Example 1

About 49.2 parts by weight of a bisphenol A dicyanate ester (BADCY, available from Lonza Ltd.) having a melting point of about 79°C, a viscosity at 80°C of about 35 MPa·S, a specific gravity at 25°C of about 1.27 g/cm³, and a cyanate equivalent weight of about 139 is dissolved in a mixture of about 47.1 parts of acetone and about 143.6 parts of brominated epoxy resin (Component B). Based upon the total weight of the mixture, about 0.03% of a catalytic solution of manganese octoate (6% active manganese) in mineral spirits and 0.07% of 2-MI under room temperature conditions are added thereto, and then the resulting mixture is stirred for about 2 hours until homogeneous.

A glass fabric is then impregnated with the resulting blend mixture and cured at 177°C for 15 minutes with about 1.38 MPa pressure, and then for about 1 hour at 220°C under the same pressure conditions.

Comparative Example 2

About 58.1 parts of bisphenol A dicyanate ester from Comparative Example 1 is dissolved in a mixture of about 54.4 parts by weight of acetone, about 109.1 parts of brominated epoxy polymeric material (Component B), and about 18.3 parts of tetrafunctional epoxy resin (Component C). About 0.024% by weight of a catalytic solution of manganese octoate (6% active manganese) in mineral spirits and 0.064% of 2-MI by weight is added thereto under room temperature conditions, and the resulting mixture is stirred for about 2 hours until

homogeneous.

A glass fabric is then impregnated with the resulting blend and cured in the same manner and under the same conditions described in Comparative Example 1.

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Comparative Example 3

About 62.4 parts by weight of bisphenol A dicyanate ester from Comparative Example 1 is dissolved in a mixture of about 41 parts of acetone, about 117.4 parts of brominated epoxy polymeric material (Component B) and about 19.3 parts of tetrafunctional epoxy resin (Component C). About 0.04% of the catalytic solution of Comparative Example 2 is added thereto, then the resulting mixture is stirred for about 2 hours until homogeneous.

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A glass fabric is then impregnated with the resulting blend and cured in the same manner and under the same conditions described in Comparative Example 1.

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The thermal, electrical, and moisture absorption properties of laminates described in Examples 1, 2, and 3 and Comparative Examples 1, 2, and 3 are illustrated in Table III.

Table III

Property	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3
T _g (TMA), °C	200	245	225	182	168-174	208-220
T _g (DSC), °C	208	222	218	170-172	183-185	206-207
UL94 Flame Rating	V0	V0	V0	V0	V0	V1
Dielectric Constant @ 1 MHz	4.88	4.32	4.54	4.29	4.26	4.30
Dissipation Factor @ 1 MHz	0.0128	0.0150	0.0158	0.0112	0.0119	0.0139
% Water Absorption D24/23°C	0.25	0.33	0.37	0.25	0.35	0.38
D24/100°C	0.66	0.99	0.92	0.89	1.21	1.49

It can be seen from Table III that substrates coated with the blend of the present invention have excellent thermal, electrical, and moisture absorbance properties. In particular, the glass transition temperature and the water absorption properties possessed by the multicyanate ester-containing blend of the present invention are superior to those properties possessed by prior art compositions employing a bisphenol A dicyanate ester. Further, as the amount of multicyanate ester in the blend of the present invention is increased, the glass transition temperature and other mechanical properties will also increase.

Example A: Blend of PT Resin With Tetrafunctional Epoxy Resin

About 202.7 parts by weight of a PT-30 resin (Component A) and about 202.7 parts of a tetrafunctional epoxy resin (Component E) are combined in a 500

ml beaker. The beaker is heated in an oil bath at ambient pressure for about 20 minutes until the temperature of the mixture is about 75°C, while the mixture contained therein is simultaneously stirred until homogeneous. About 0.2 parts of a catalytic solution (Component H) was added thereto, and the resulting mixture is stirred until the catalyst completely dissolves.

The resulting blend is poured into a 20.3 cm x 17.78 cm x 0.32 cm glass mold preheated to about 80°C, which was pretreated with a silicone release agent available from Chemlease Inc. under the tradename "Chemlease 70", and then the filled mold is degassed in a vacuum oven set at about 70°C to 80°C with about 4000 Pa vacuum pressure (30 torr). After 18 hours of curing at 120°C, the sample is removed from the glass mold and postcured for another 30 minutes at 150°C, 105 minutes at 180°C, 30 minutes at 200°C, followed by 4 hours at 220°C.

Example B: Blend of PT Resin With Epoxy Novolac Resin

About 200 parts of a PT-30 resin (Component A) and about 200 parts of an epoxy novolac resin (Component F) are combined in a 500 ml beaker, which was heated in the same manner and under the same conditions described in Example A. About 0.22 parts of the catalytic solution of Example A was added thereto, then the resulting mixture is degassed and molded in the manner described in Example A. After 18 hours of curing at 120°C, the sample was removed from the glass mold and post cured for another 0.5 hours at 150°C, 2 hours at 180°C, 0.5 hours at 200°C, followed by 4 hours at 220°C.

Example C: Blend of PT Resin With Bis A Type Epoxy Resin

About 174.9 parts of a PT-30 resin (Component A) and about 174.9 parts

of a bisphenol A type epoxy resin (Component G) are combined in a 500 ml beaker, which is heated in the same manner and under the same conditions described in Example A. About 0.20 parts of the catalytic solution of Example A is added thereto in the manner described in Example A. The resulting mixture is molded and cured in the manner described in Example A.

Comparative Example A

The PT resin of Example A is replaced with about 47 parts of the bisphenol A dicyanate of Comparative Example 1. Then, 53 parts of a tetrafunctional epoxy resin (Component E) is added thereto according to the method described in Shimp et al., "Co-Reaction of Epoxide and Cyanate Resins", 33rd Int'l SAMPE Symposium and Exhibition 1-13 (Calif. March 7-10, 1988).

Comparative Example C

The PT resin of Example C is replaced with about 57 parts of the bisphenol A dicyanate of Comparative Example 1. Then, 43 parts of an epoxy resin (Component G) is added thereto according to the method described in Shimp, "AroCy® Cyanate Ester Resins Chemistry, Properties & Applications," (3rd Edition, May 1991).

The thermal, electrical, and moisture absorption properties of the blends described in Examples A, B, and C and Comparative Examples A and C are illustrated in Table IV.

Table IV

	Ex. A	Comp. Ex. A	Ex. B	Ex. C	Comp. Ex. C
Cure Temp., °C	220	235	220	220	200
Properties					
HDT, °C		237			190
T _g (DMA), °C	273.7		216.7	221.6	
T _g (TMA), °C	291.3		185.8	263.4	
Flexural Strength, ASTM D790 MPa	90	73	87	126	132
Flexural Modulus GPa	3.9	3.0	3.8	3.7	2.8
Elongation, %	2.4	2.1	2.4	3.81	5.3
Dielectric Constant at 1 MHz	3.39	3.3	3.0	3.17	3.1
Dissipation Factor at 1 MHz	0.0181 4	0.017	0.0133 3	0.0246 3	0.013
H ₂ O Absorption, % (ASTM D570)	0.47 ^(a)	2.1 ^(b)	0.36 ^(a)	0.32 ^(b)	1.2 ^(a)
Compressive Strength, MPa	339		331	265	
Compressive Modulus, GPa	2.8		2.6	2.4	

(a) Immersed in RT water for 24 hours. (b) Conditioned 64 hours at 92°C and >95% RH.

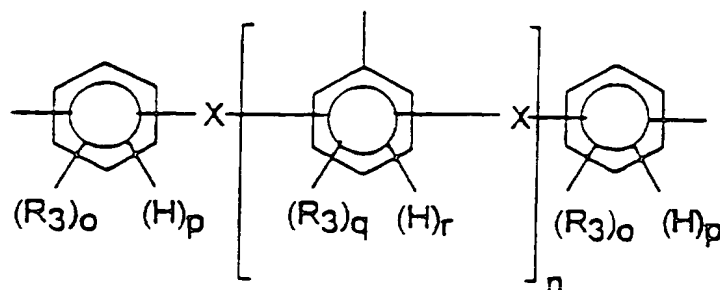
"HDT", as used herein, refers to heat distortion temperature, which for purposes herein, is comparable to the glass transition temperature (" T_g "). It can be seen in Table IV that the blend of the present invention has a higher T_g and an improved water absorption than those of the prior art dicyanate ester-epoxy blends. This is because the multifunctional cyanate esters of the present invention possess greater than two cyanate groups, which results in blends having a greater percentage of cured bonds and thus upon subsequent reaction, a greater percentage of triazines. The presence of a large amount of triazines contributes to a higher T_g and a lower water absorption.

We claim:

1. A blend comprising:

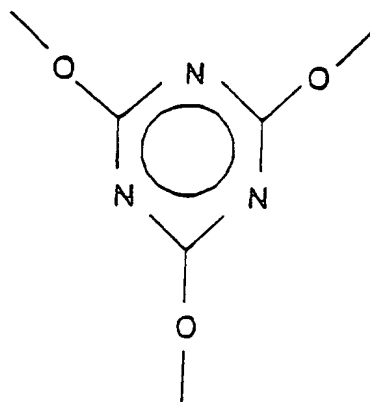
a) a multifunctional phenolic cyanate/phenolic triazine copolymer

comprising three or more phenolic moieties of formula I:



I.

linked by way of at least one of the open valences to one or more triazine moieties of the formula II:



II

and wherein the remainder of the open valences of said phenolic moieties are substituted with -OH, -OCN, or other triazine moieties, provided that at least one of said remaining open valences is substituted with a -OCN moiety; wherein:

n is a positive whole number equal to or greater than 1;

q and r are the same or different at each occurrence and are whole

numbers from 0 to 3 with the proviso that the sum of q and r at each occurrence is equal to 3;

o and p are the same or different at each occurrence and are whole numbers from 0 to 4, with the proviso that the sum of o and p is equal to 4;

-X- is a divalent organic radical; and

R₃ is the same or different at each occurrence and is a substituent other than hydrogen which is unreactive under conditions necessary to completely cure the copolymer; and

b) an epoxy resin.

2. The blend of Claim 1 wherein said blend comprises, based upon the total weight of the blend, from about 5 to about 95 percent of said multifunctional phenolic cyanate/phenolic triazine copolymer and from about 5 to about 95 percent of said epoxy resin.

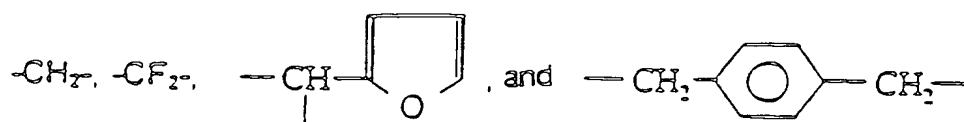
3. The blend of Claim 2 wherein said blend comprises, based upon the total weight of the blend, from about 15 to about 50 percent of the multifunctional phenolic cyanate/phenolic triazine copolymer and from about 25 to about 70 percent of said epoxy resin.

4. The blend of Claim 1 wherein the amount of phenol groups in said copolymer is, based upon the total mol percent of multifunctional phenolic cyanate/phenolic triazine copolymer, from about 2 to about 25 mol percent.

5. The blend of Claim 1 wherein up to about 90 mol percent of the phenyl groups in said copolymer are substituted with -OCN groups, said mol content based on the total mols of phenyl groups in said copolymer.

6. The blend of Claim 1 wherein X is substituted or unsubstituted methylene or 1,4-benzenedimethylene, wherein permissible substituents are alkyl having from 1 to about 10 carbon atoms, halo, and furyl.

7. The blend of Claim 6 wherein X is a moiety selected from the group consisting of:



8. The blend of Claim 1 wherein n is from about 1 to about 20.

9. The blend of Claim 8 wherein n is from about 3 to about 10.

10. The blend of Claim 1 wherein:

o is 0 or 1;

p is 3 or 4;

q is 0 or 1; and

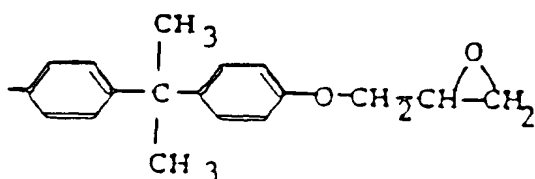
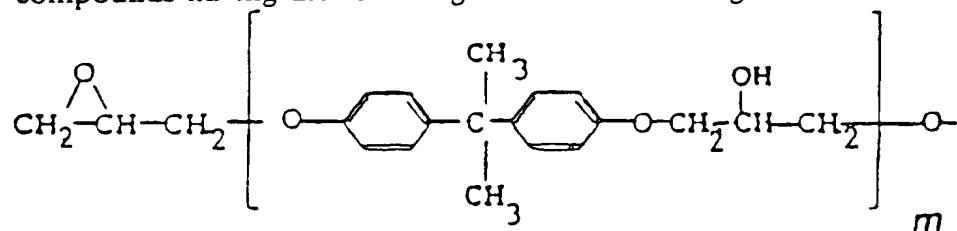
r is 2 or 3.

11. The blend of Claim 1 wherein R₃ is methyl or ethyl.

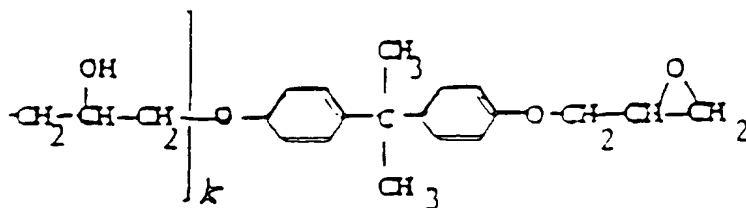
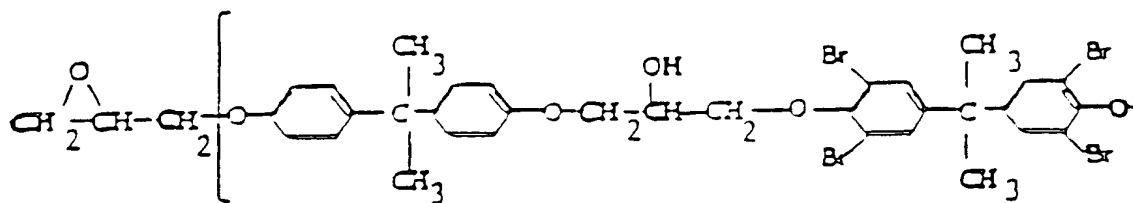
12. The blend of Claim 1 wherein said epoxy group of component b is selected from the group consisting of bisphenol A based epoxy resins, halogenated epoxy resins, epoxy novolac resins, polyglycol epoxy resins, multifunctional epoxy resins and mixtures and copolymers thereof.

13. The blend of Claim 1 wherein said epoxy group is selected from the

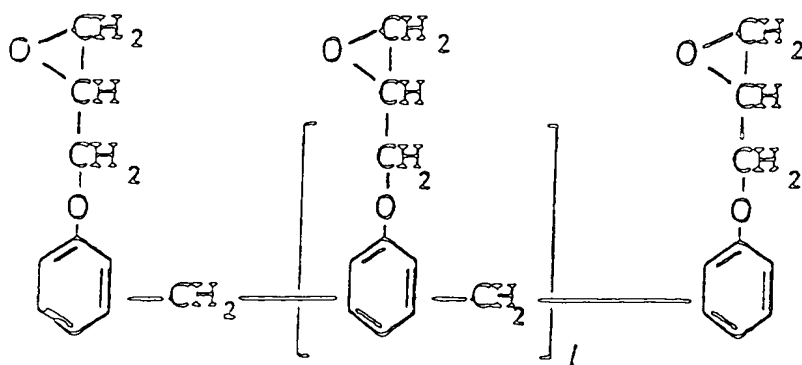
compounds having the following formulas consisting of:



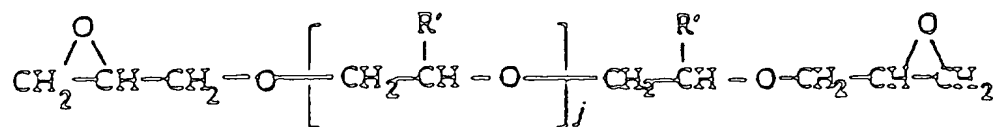
wherein the average value of m is from about 0.1 to about 1,



wherein the average value of k is from about 2 to about 3,

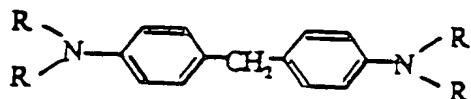


wherein the average value of *l* is from about 0.1 to about 2,

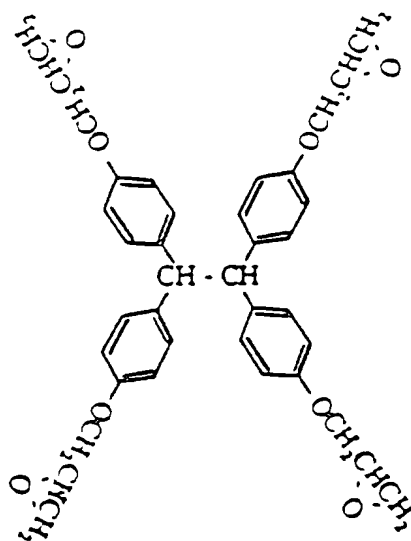


wherein the average value of *j* is about 1 to about 2 and R' is an organic group or
 5 hydrogen, tetra-functional epoxy resins, tri-functional epoxy resins, and mixtures
 and combinations thereof.

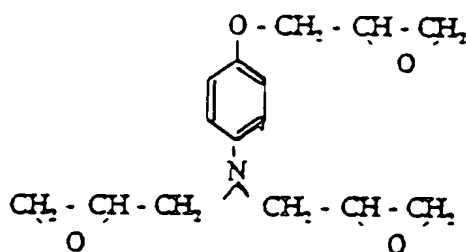
14. The blend of Claim 12 wherein said tetrafunctional epoxy resin is



wherein R is $\text{CH}_2-\text{CH}-\text{CH}_2$ (with an oxygen atom bridging the two CH groups), or



and said trifunctional epoxy resin is



15. The blend of Claim 12 wherein said halogenated epoxy has, based upon the total weight of the epoxy resin, from about 15 percent to about 45 percent halogenation.

16. The blend of Claim 15 wherein said halogenated epoxy has, based upon the total weight of the epoxy resin, from about 8 percent to about 12 percent halogenation.

17. The blend of Claim 1 further comprising, based upon the total weight of the blend, from about 0.08 to about 0.11 percent of at least one catalyst.

18. The blend of Claim 17 wherein said catalyst is selected from the group consisting of lead naphthenate, manganese naphthenate, manganese octoate, manganic acetylacetonate, cobalt octoate, cobalt naphthenate, cobalt acetylacetonate, zinc octoate, zinc naphthenate, zinc acetylacetonate, copper acetylacetonate, cupric naphthenate, nickel acetylacetonate, titanyl acetylacetonate, ferric octoate, tin octoate, diazabicyclo-[2.2.2]-octane, catechol, 1,1-dimethyl-3-phenylurea, nonylphenol, 1-methylimidazole, 2-ethyl-4-methylimidazole, 2-phenylimidazole, 2-methylimidazole, and mixtures thereof.

19. The blend of Claim 17 wherein said catalyst is selected from the group consisting of manganese octoate and 2-methylimidazole.

20. The blend of Claim 19 further comprising, based upon the total weight of the blend, from about 0.01 to about 1 percent of a curing agent selected from the group consisting of a metal catalyst and 2-methylimidazole.

21. The blend of Claim 2 further comprising, based upon the total weight of the blend, up to about 20 percent of a multifunctional epoxy resin component in addition to the epoxy resin of component b.

22. The blend of Claim 2 further comprising, based upon the total weight of the blend, from about 5 percent to about 10 percent of a multifunctional

epoxy resin component in addition to the epoxy resin of component b.

23. The blend of Claim 1 which has a glass transition temperature of at least about 200°C and a flexural strength of at least about 90 MPa.

24. The blend of Claim 1 which has flexural modulus of at least about 3.7 GPa and a water absorption rate of about 0.32% water immersion after 24 hours at room temperature.

25. The blend of Claim 1 further comprising one or more additives selected from the group consisting of solvents, fillers, mold release agents, pigments, dyes, flow modifiers, coloring pigments and mixtures thereof.

26. An article resulting from curing a blend of Claim 1 blended with a curing quantity of at least one curing agent, catalyst, or mixture of curing agent and catalyst therefor.

27. The article of Claim 26 wherein said article is a rigid substrate suitable for the production of printed circuit board.

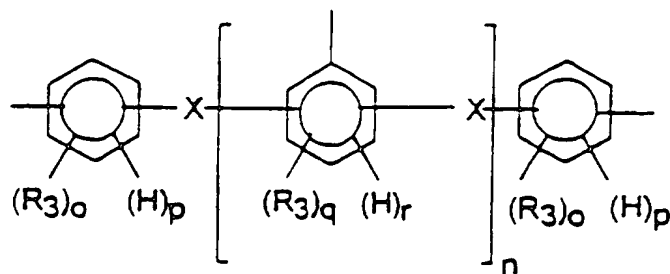
28. A preimpregnated substrate comprising a reinforcing material impregnated with the blend of Claim 1 blended with at least one curing agent, catalyst, or mixture of curing agent and catalyst therefor.

29. A laminate or composite material comprising at least one ply of the preimpregnated substrate of Claim 28.

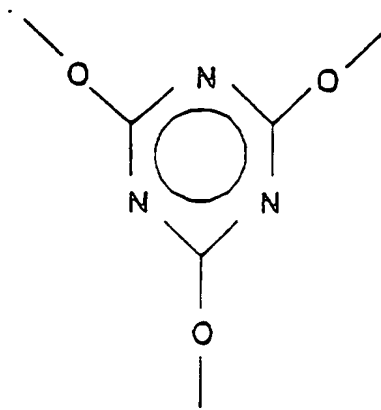
30. An electrical laminate comprising at least one ply of the preimpregnated substrate of Claim 28 and at least one outer ply of an electrical conducting material.

31. A blend comprising, based upon the total weight of the blend,

a) from about 15 percent to about 50 percent of a multifunctional phenolic cyanate/phenolic triazine copolymer comprising three or more phenolic moieties of formula I:



linked by way of at least one of the open valences to one or more triazine moieties of the formula II:



and wherein the remainder of the open valences of said phenolic moieties are substituted with -OH, -OCN, or other triazine moieties, provided that at least one of said remaining open valences is substituted with a -OCN moiety; wherein:

n is about 3 to about 10;

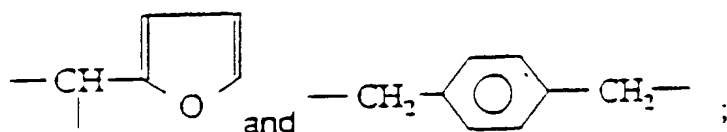
from, based upon the total mols of phenyl groups in said copolymer, about

5 to about 20 percent of the phenyl groups of said copolymer are substituted with -OCN groups and from about 5 to about 20 percent of said phenyl groups are substituted with -OH groups;

q is 0;

o is 0;

X is a moiety selected from the group consisting of $-\text{CH}_2-$, $-\text{CF}_2-$,

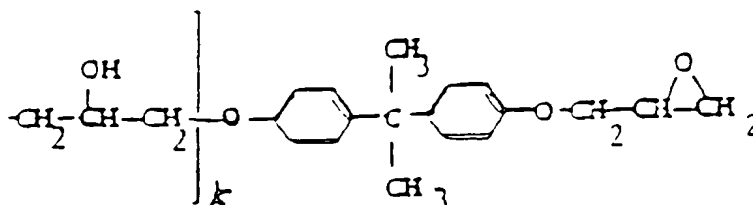
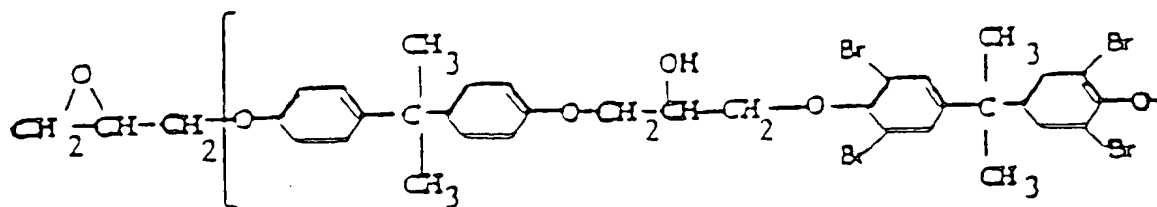


r is 3;

and p is 4; and

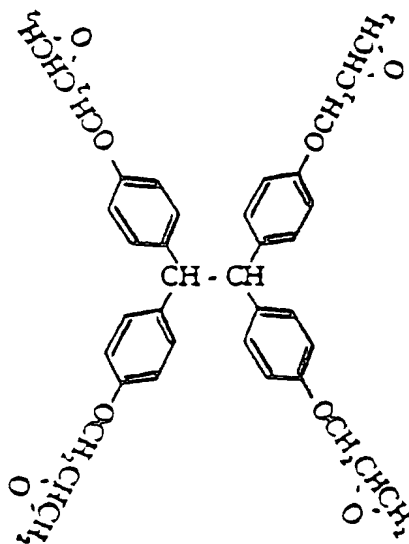
R_3 is the same or different at each occurrence and is a substituent other than hydrogen which is unreactive under conditions necessary to completely cure the copolymer; and

b) from about 25 percent to about 70 percent of a brominated epoxy resin having the formula



wherein the average value of k is from about 2 to about 3, said brominated epoxy resin comprising, based upon the total weight of said brominated epoxy resin, from about 50 percent to about 70 percent bromination;

c) from about 5 to about 10 percent of a tetrafunctional epoxy resin having the formula

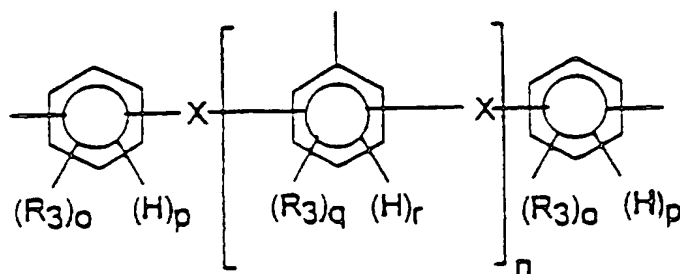


d) from about 0.01 percent to about 1 percent of a manganese octoate catalyst; and

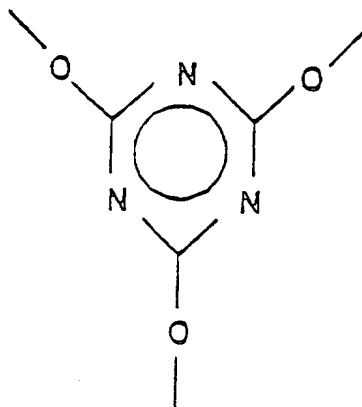
e) from about 0.5 percent to about 1 percent of a 2-methylimidazole curing agent.

32. A blend comprising, based upon the total weight of the blend,

a) from about 15 percent to about 50 percent of a multifunctional phenolic cyanate/phenolic triazine copolymer comprising three or more phenolic moieties of formula I:



linked by way of at least one of the open valences to one or more triazine moieties of the formula II:



II

and wherein the remainder of the open valences of said phenolic moieties are substituted with -OH, -OCN, or other triazine moieties, provided that at least one of said remaining open valences is substituted with a -OCN moiety; wherein:

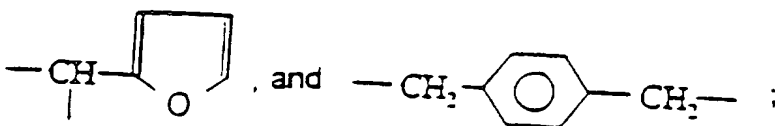
n is about 3 to about 10;

from, based upon the total mols of phenyl groups in said copolymer, about 5 to about 20 percent of the phenyl groups of said copolymer are substituted with -OCN groups and from about 5 to about 20 percent of said phenyl groups are substituted with -OH groups;

q is 0;

o is 0;

X is a moiety selected from the group consisting of -CH₂-, -CF₂-,

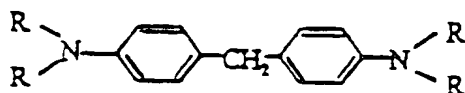


r is 3;

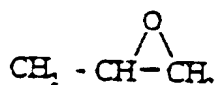
and p is 4; and

R_3 is the same or different at each occurrence and is a substituent other than hydrogen which is unreactive under conditions necessary to completely cure the copolymer; and

b) from about 25 percent to about 70 percent of an epoxy having the formula



wherein R is



wherein said blend has a glass transition temperature of at least 200°C and a water absorption rate of about 0.32% water immersion after 24 hours at room temperature.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 95/14560

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L79/04 C08L63/00 C08G59/40 //(C08L79/04,63:00),
(C08L63/00,79:04)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 544 704 (HEFNER, JR.) 1 October 1985 see claims 1,5 ---	1-32
A	WO,A,87 04443 (ALLIED CORPORATION) 30 July 1987 see claims 1-42 & US,A,4 970 276 cited in the application ---	1-32
A	DE,A,40 22 255 (AKADEMIE DER WISSENSCHAFTEN DER DDR) 24 January 1991 cited in the application see claims 1,2 -----	1-32

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

18 March 1996

Date of mailing of the international search report

19. 04. 96

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Authorized officer

Glanddier, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/US 95/14560

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4544704	01-10-85	NONE	
WO-A-8704443	30-07-87	DE-A- 3786662	26-08-93
		DE-T- 3786662	04-11-93
		EP-A,B 0290458	17-11-88
		JP-T- 1501481	25-05-89
		US-A- 5426161	20-06-95
		US-A- 4978727	18-12-90
		US-A- 4970276	13-11-90
		US-A- 5124414	23-06-92
		US-A- 5130385	14-07-92
DE-A-4022255	24-01-91	NONE	

